

UNITED STATES AIR FORCE
RESEARCH LABORATORY



NOVEL, FULL COLOR FLAT PANEL DISPLAY
TECHNOLOGY EMPLOYING HIGH PERFORMANCE,
CRYSTALLINE ORGANIC SEMICONDUCTOR
LIGHT EMITTING DIODES

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This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER



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13. ABSTRACT (Maximum 200 words) During the course of this program, several breakthroughs in the development of full color flat panel displays based on organic light emitting devices (OLEDs) were made. In particular, we demonstrated the first transparent OLED, flexible OLED based on molecular organic materials, and full color stacked OLED. These three devices, along with several other similar structures, including high efficiency devices employing "shaped substrates" and inverted, integratable OLEDs, provide a range of tools which change the possibilities for realizing very high resolution, high efficiency, and light-weight OLED based displays for a wide range of DOD and commercial applications. In other advances, we developed a model linking current transport and electroluminescence in molecular OLEDs, and have worked closely with several industrial partners to rapidly transfer technology from the conceptual, laboratory phase into commercial applications.					
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Section 1:

Summary of Overall Accomplishments During the Contract Period

- **Basic Understanding of OLED Operation.** The first consistent model to describe current transport and electroluminescence in OLEDs within the same theoretical framework was developed. The model is now generally accepted by researchers in the field, and our early publications are widely cited. This basic understanding allowed for optimization of the OLED structure.
- **A Package for OLEDs** was developed to protect them from atmospheric degradation. Princeton was the first group to publish systematic work on OLED degradation and show a commercially-useful OLED lifetime.
- **Developed transparent contacts for OLEDs.** The foundation of our strategy for developing novel full color displays was the proprietary stacked OLED (SOLED). Realization of efficient transparent contacts was a crucial first vindication of the viability of SOLED technology.
- **Demonstrated Stacked OLEDs.** Initially two-color, and later three color SOLEDs were fabricated and tested for high resolution display applications. Seven segment color-tunable displays were demonstrated based on the two-color SOLED. Detailed analysis and optimization of the SOLED structure for saturated color, high resolution displays was undertaken.
- **Inverted OLEDs**, compatible with n-channel Si-MOSFET technology, were demonstrated using an inverted layer structure. These devices enhance the ease of integration of OLEDs with Si, since p-channel drivers, required for conventional OLED structures, are currently unavailable in amorphous silicon.
- **A Technique for Screening New Compounds** was developed, based on measuring the absolute PL and EL efficiency.
- **High Efficiency OLEDs** on shaped substrated were demonstrated, redirecting light which would normally be waveguided to increase the device efficiency by a factor of two.
- **New Materials** for enhanced red light emission, and hole transporting materials with improved thermal stability were developed (with USC).
- **Technology Transfer** was rapid and successful, with staff from Hughes and Universal Display Corp. spending extended periods at Princeton to learn OLED and TOLED technology, and practice preparing, handling and packaging OLEDs and TOLEDs.
- **Prototyping Scale-up** was quickly implemented at Princeton, with the building of a 1000 square foot OLED prototyping facility, with class 100 substrate preparation and 4" diagonal display fabrication ability. Beginning in early 1997, three UDC researchers worked full-time on the development of this facility.
- **Intellectual Property** was aggressively pursued, with over 30 US patents currently filed, two of which have been allowed. The entire patent portfolio is exclusively licensed to UDC.

Section 2:

Final Technical Report

S.R. Forrest, Princeton University

(Reports of our major accomplishments are either published in the scientific literature or submitted for publication. A list of references is attached in Section 5 and should be consulted for further technical details.)

Probably the most fast-moving display technology today is organic electroluminescent devices (OLEDs). These thin film displays (the active layers are about 1/1000th the thickness of a human hair) were first demonstrated in their present form just over ten years ago. A state-of-the-art OLED now emits light several times brighter than a conventional CRT display and works for several tens of thousands of hours at a voltage of less than 10 V. Such characteristics are extremely attractive for flat panel display applications.

This work was motivated by the unique properties of organic light emitters which may make possible new display applications. In particular, the high transparency of the organic thin films over the visible spectral region led to a proposal for transparent OLEDs (TOLEDs). Three different color TOLEDs may then be built sequentially on top of one another. Each device in the stack is independently addressable using external current sources, and emits its own color through the transparent organic layers, the transparent contacts and the substrate, allowing the entire device area to emit any combination of the three colors, as shown in Fig. 1. This stacked OLED (or SOLED) may replace the conventional architecture for fabricating full color displays, where red, green and blue pixels are separately patterned in a side-by-side (SxS) geometry. As long as the observer is too far from the SxS display to resolve the separate color pixels, the illusion of a full-color display is created. The need for at least three pixels at each point in the display, however, limits its resolution and, for close-up viewing (such as for a head-mounted display), extremely small pixels may be required to maintain the illusion. In contrast, each pixel in a SOLED display is intrinsically color-tunable by addressing the vertically-stacked sub-pixels. This effectively triples the resolution of the display, while also cutting down on the amount of dark space in between the pixels. As an added bonus, since the three colors are vertically stacked in a co-axial geometry, the SOLED offers full color at any resolution or viewing distance,- there are no SxS sub-pixels for the eye to resolve.

Figure 1: Schematic cross-section of a three-color SOLED

The weak nature of the so-called van der Waals forces responsible for the inter-molecular bonding in organic materials leads to a property unobtainable with conventional displays: OLEDs can be deposited on thin, flexible, plastic substrates to make large conformable, flexible, or even roll-up flat panel displays which can range in size from the miniature, for example personal digital assistants, to wall-size displays. Both the OLEDs and the plastic substrates are so light that the weight of a computer monitor could in principle be reduced to a mere few ounces.

The contract aimed to accomplish the following milestones, as laid out in the revised statement of work, June 28 1995:

- Optimize the discrete, single-color OLEDs for structural stability, high brightness and color purity.
- Demonstrate semi-transparent contacts for OLEDs
- Demonstrate a full-color, compact, integrated OLED pixel.
- Transfer technology to industrial partners and work closely with the appropriate manufacturing development groups.
- Begin scale-up of technology to larger arrays of OLED pixels.

2.1 Discrete OLED Optimization.

The key to optimization of the complex OLED layer structure [23] is the understanding of the processes limiting current conduction and electroluminescence. To this end, we developed a comprehensive theory of trap-limited conduction (TCL) in the luminescent layer of OLEDs [4,5]. The TCL model was based on the results of an extensive investigation into the dependence of current on applied voltage and of luminance on injected current in OLEDs with systematically varied layer thicknesses and over a wide range of temperatures. This model, which has since become generally accepted and widely referenced, allows for understanding the origin of electroluminescence in OLEDs, and for optimization of various parameters such as doping concentration in guest-host doped devices. The semi-empirical computer package ZINDO was used for the first time to model transport in organics and pinpoint the origin of recombination in Alq₃ [5]. Further understanding of how to tune the emission color of organic molecules was also derived [5].

Having understood the mechanism of electroluminescence (EL) generation, we sought to identify and control external loss mechanisms such as waveguiding of light in the substrate and organic layers. Quantification of these losses revealed that four out of every five photons emitted from an OLED were in fact lost, largely due to internal reflection and waveguiding in the substrate and organic layers [11]. With improved design and a shaped substrate, these effects were reduced to yield a *factor of two efficiency increase* [12]. Subsequent design improvements predict an attainable *factor of four efficiency increase*, without necessitating any improvement in the fluorescence efficiency of the organic layers of the OLED.

A spin-off invention based on this work was a means to improve the efficiency of conventional silicon solar cells using a fluorescent anti-reflection coating of organic material similar to that used in OLEDs [11]. The same work also yielded an efficient method for quantifying the absolute PL and EL efficiencies of new materials [11].

Further work to optimize discrete, single color OLEDs involved substantial research into new materials to replace the well-known luminescent Alq₃ and the hole-transporting TPD. A critical problem with TPD in particular was its low glass transition temperature of

65°C. Above this temperature, recrystallization of the TPD resulted in rapid and irreversible device failure. Working with USC, we have characterized new asymmetric hole-transporting materials which increase this catastrophic failure temperature up to 130°C. We also invested considerable effort into generating new materials with improved red emission, and demonstrated the red emitting OLEDs with both high quantum efficiency and narrow spectral linewidth (i.e. high color purity). These improvements made possible the first 2 color SOLED, with good color-separation between the independent color elements (Sect. 2.4). Further details of the materials aspects of our work are contained in the USC report, Section 3.

In all our materials work and chemistry collaboration with USC, we have focussed on systematic studies of classes of molecules, and attempted to relate the electroluminescent properties of new materials to their molecular structure, such as with the penta-co-ordinated gallium chelates [8] attached in Appendix A.8

2.2 Transparent Contacts For OLEDs

We developed a proprietary, low power radio-frequency sputtering technique for depositing transparent contacts on organic thin films (U.S. patent allowed and expected to issue shortly, see Sect. 3). This was a *crucial enabling technology* for our full-color stacked OLED architecture. The substrate, indium tin oxide (ITO) anode and organic layers are highly transparent across the visible spectral range. The top cathode, however, conventionally consists of MgAg alloy, which is both opaque and highly reflective (the latter property killing display contrast in high ambient light environments).

It was proposed to build a *totally transparent* light emitting pixel by using ITO as a transparent cathode. Since ITO can not be easily deposited by thermal evaporation, a vacuum chamber dedicated for radio-frequency sputtering was designed and built. A stable, low-voltage cathode was obtained by first depositing a thin (100 Å) layer of MgAg alloy (to enhance electron injection) which was capped with ITO deposited by sputtering at room temperature [6,7]. Typical transparency of TOLEDs is 70% across the visible spectral range

Improvements in reproducibility of TOLEDs at Princeton allowed creation of transparent, 4 character, multi-segment alphanumeric display, an example of which was delivered to Mark Hartney at DARPA. Transfer of TOLED technology to Hughes was effected, and several extended visits of Hughes personnel to Princeton led to creation by Hughes staff of 8 x 12 matrix of TOLEDs, the first direct-drive transparent pixellated display. Staff members from Universal Display Corporation have also received training in TOLED fabrication at Princeton.

In the most recent quarter, we have reported the development of totally transparent TOLEDs with the elimination of metal in cathode [20]. The implications of this improvement are enormous, since the metal-free device structures also show very low reflectivity, making them highly applicable to high-contrast display applications, or for displays used under intense ambient lighting (such as airplane cockpits), where reflection from a conventional display would substantially reduce its contrast ratio. The low reflectivity will also make possible improvements in the stacked OLED by eliminating color-shifts induced by microcavity effects.

2.3 Degradation of OLEDs.

The Princeton Group was the *first to systematically examine* environmental impact on OLEDs [1], discovering that atmospheric degradation was dominant in unencapsulated devices.

Until this point, there was no clear evidence that OLEDs could be made with commercially useful operating lifetimes. We also developed a simple epoxy package [1] which improved the lifetime (to 50% brightness) of OLEDs to 1000hr, the longest published OLED lifetime at that time. Subsequent work increased this to 4000 hr, and recent publications by other groups suggest the potential for at least 20,000 hour OLEDs.

We have recently completed the building of a computerized lifetime testing station, which allows unattended stress testing of up to 60 independent devices. Preliminary results on the reliability of our TOLEDs suggest that these devices have *longer lifetimes* than equivalent, conventional OLEDs. We currently believe that this improved lifetime is due to the elimination of most of the reactive Mg from the TOLED cathode. Further work is underway to clarify this relationship, and will be continued into phase 2 of the program.

2.4 Full-Color Stacked OLEDs.

After the realization of the enabling TOLED technology, we quickly demonstrated the first independently tunable, two-color stacked OLED (SOLED), tunable from blue to red [10]. One of the primary deliverables of this contract, a three-color SOLED, was developed soon thereafter. This device was published in "Science" [16] and attracted widespread industry attention, with write-ups in several popular science and technology magazines and newspapers, including "Business Week."

Analysis of the working SOLED [16] confirmed several characteristics *crucial for its application to full-color displays*:

- Output from each individual SOLED element was linear in current.
- No cross-pumping (color-bleeding) of the red element by the blue element was observed.
- The output spectrum of the SOLED was a linear superposition of spectra from the three separate color elements.

With these features demonstrated, a full color, SOLED-based display was shown to be feasible, with independent control over color, brightness and greyscale.

Detailed analysis of the SOLED characteristics revealed unexpected microcavity effects, which appear as color shifts in the spectra of the individual elements. Further work developed way to optimize the device structure, harnessing these effects to improve the color-purity of the output light [17].

2.5 Si-Integratable OLEDs.

Conventional OLEDs are built in an anode-down configuration, requiring a transparent substrate for light emission, and a p-channel MOSFET driver. This raises problems for integration of OLEDs with Si-based drive circuits. Firstly, a low temperature process is required to deposit Si transistors onto the transparent (usually glass) OLED substrate. This would suggest the use of low-temperature amorphous Si, however p-channel technology does not yet exist in amorphous Si, and the relatively low mobility of even state-of-the-art amorphous silicon *may not be sufficient for these current-driven devices*. Various solutions to this problem include complex transfer techniques to place crystalline Si devices made elsewhere onto glass or plastic OLED substrates.

Our proprietary TOLED structure, however, does not require a transparent substrate, since light is emitted though the top, transparent cathode. Therefore these devices offer the potential for easy integration onto crystalline Si wafers (where p-channel technology is well-known), particularly for small, ultra-high resolution displays suitable for head-mounting. We also demonstrated an inverted OLED structure (cathode-down) using a transparent crystalline

organic protection layer beneath a sputtered ITO top anode [13]. Such a device is applicable to direct driving by n-channel FETs.

2.6 Flexible Lightweight OLEDs

Although not part of the original workplan, we accomplished the first successful demonstration [9] of flexible OLEDs (FOLEDs) grown on commercially-available, 150 μ m thick polyester sheets pre-coated with ITO. This required solving problems of how to clean solvent-sensitive plastic substrates to sufficiently high standards for growth of organic thin films. We also demonstrated TOLEDs grown on similar substrates [14]. The limits to flexibility (~8 mm radius of curvature) and failure modes were investigated.

FOLED technology offers the potential for extremely lightweight and rugged displays, as well as for easy fabrication of displays on curved surfaces such as cockpits and helmet visors. As such, they form a significant part of our phase 2 continuation.

2.7 Technology Transfer

Technology transfer from Princeton to our industrial partners was rapid and successful throughout the lifetime of the contract. In the initial phase of technology transfer to Hughes, two of their researchers spent several extended periods at Princeton learning OLED technology. This led to the production at Hughes of small, packaged logo displays which were evaluated by Delco (details in the Hughes final report, Sect. 4). Hughes staff were also taught our TOLED technology, including the details of making transparent electrode contacts to delicate organic thin films. With this knowledge, and working largely in Princeton facilities, they were able to fabricate 8x12 arrays of TOLED pixels, which we believe to be the world's first pixellated transparent display. Researchers from Hughes also completed a study of device lifetime, using OLEDs grown at Princeton on substrates prepared at Hughes facilities in Malibu, CA.

From year 2, we also developed extensive contacts with Universal Display Corporation (UDC), based in Bala Cynwyd, PA, leading to a formal collaboration in Phase 2 of the project. Currently, three UDC staff work full-time in new Princeton OLED prototyping facility, learning our technology and working with us to improve aspects of device performance and packaging (such as new packaging materials). We have completed transfer of our OLED fabrication, TOLED fabrication and packaging technologies to UDC personnel, who have worked with us to fabricate 4-character alphanumeric displays with red, blue and green light emitters, and transparent alphanumeric displays. Recently, UDC staff have designed and fabricated at Princeton a large (4" diagonal) multi-pixel green alphanumeric display, which has been packaged into a prototype cellphone by Lucent Technologies. In the next year, UDC have committed to building an independent prototyping facility for further scale-up of technology in NJ.

Princeton also hosted staff from Xerox corporation, who are studying the application of our high-efficiency OLED technology [12] to low-cost printing applications.

2.8 Prototyping Scale-up.

In the second half of the contract, we began work on scale-up of our prototyping facilities, using knowledge gained in 1st 18 months. We designed a larger scale (4" substrate diagonal) integrated thermal deposition and glovebox system for OLED deposition. This system, completed and now fully operational, is capable of scaling prototyping to 4" diagonal, 1/4VGA displays.

In addition, our work on reliability and degradation of OLEDs yielded the following important information:

- Dust contamination on the substrate prior to organic film growth is lethal to device performance, nucleating "dark spot" defects [1] which then grow uncontrollably as the device is operated.
- Atmospheric contamination of the grown organic thin film, particularly by water vapor, contributes significantly to device degradation both during operation and storage.

To eliminate both of these undesirable effects, we further expanded our prototyping laboratory. To reduce dust contamination, we constructed a 500ft² class 100 cleanroom for OLED substrate fabrication. Construction is now complete, all processing equipment is installed and the cleanroom is expected to be fully operational within one month. To eliminate atmospheric contamination during the OLED growth process, and to allow for the fabrication of 4" diagonal TOLED displays, we have designed and ordered a large-area rf sputtering system for top cathode deposition, to be integrated with the existing thermal evaporator in the new facility. This will allow for the fabrication of packaged TOLEDs and SOLEDs *without any exposure to the atmosphere* for the first time. The sputtering chamber is expected to be delivered within a month, and the entire system will be operational by the end of the year.

In addition to prototyping scale-up, the new facility will be used to further transfer new technology to collaborating staff members from Hughes and UDC. UDC currently has one researcher and one technician on site working full-time in the clean-room prototyping facility, and expects to add more staff as they become formal collaborators on phase 2 of the contract.

2.9 Intellectual Property.

We have aggressively pursued OLED intellectual property for the entire contract duration, and currently have over 30 patents filed with the US patent office, two of which have been allowed and are awaiting issuance. A list of DARPA-supported patents is given in Sect. 2.12. The entire portfolio of Princeton and UDC patents have been paid for and exclusively licensed by Universal Display Corporation (UDC), which made an initial public offering of stock on the Nasdaq stock exchange in April 1996, based largely on the commercial potential of the growing Princeton/UDC patent portfolio. We expect to further expand our patent portfolio in phase 2 of the contract.

Section 3:

Final Technical Report

Mark Thompson, University of Southern California

Students supported on DARPA funds

Dennis McCarty	50%
Doug Loy	50%
Andrei Shousitkov	50%
Shannon Rice	25%
Sergey Lamansky	40%

Postdoctoral Fellows

Linda Sapochak	50%
Jon Cronin	50%
Scott Sibley	50%
Yujian You	50%

Under DARPA sponsorship we have focused on two basic areas in this program. The first involves the synthesis and study of thermally stable hole transporting materials. The second program involves the preparation of saturated red OLEDs and novel carrier materials, designed for doping with red PL dye dopants. Both of these programs are described below.

Thermally stable hole transporters

We have prepared two types of materials which behave as thermally stable hole transporting materials. These materials may have a number of uses, but their immediate application in our labs is in organic light emitting diodes. The first material to be described is a compound we have prepared and tested, abbreviated PPD. The second material described is actually a general class of materials which have been designed to have high glass transition temperatures. These compounds are asymmetric tertiary amines, which may be used neat or as crystallization inhibitors in other materials.

A well documented cause of OLED failure is thermally induced deformation of the organic layers (*e.g.* melting, glass formation, *etc.*). This failure mode can be seen in the studies that have been carried out with hole transporting materials. The most common hole transporter used in OLEDs is a biphenyl bridged diamine, TPD (Figure 1). This material has a melting point of 167°C and a glass transition temperature of 65°C. If a device prepared with TPD is heated above 65°C, catastrophic and irreversible failure results. In order to increase the glass transition temperature of the HTL, several groups have explored different modifications to the basic structure of TPD. While these studies have led to materials with T_g values as high as 150°C, they have not led to an understanding of why certain changes increase the T_g , while others may not effect it or lower it. We found that replacing the amine groups of TPD with carbazole groups (CBP

in Figure 1) increased the melting point to 285 °C, however, the material shows no glass transition. The group at Kodak as well as Sato, *et. al.*, have investigated the NPD, see Figure 1, which does make a stable glasses. The α form (1-substituted naphthyl group) has a higher T_g than TPD (105°C), while the β form (2-substituted naphthyl) is lower (55°C).**

PPD:

The molecular structure of PPD is given below. This material has a melting point of 266-268°C and a glass transition temperature of 135°C. The T_g value for PPD is 35°C higher than NPD and 65°C higher than TPD (see scheme for definitions). PPD has a complicated NMR spectrum [δ (multiplicity) in d_6 -DMSO, 7.00(multiplet), 7.24(triplet), 7.45(doublet), 7.62(multiplet), 7.77(singlet), 7.95(multiplet), 8.88(multiplet)]. Major mass spectral lines are observed at 688.1(34), 303.9(47), 221.1(18), 170.0(58), 141.0(76), 77.0(100) (values in parentheses are the relative peak intensities). OLEDs have been fabricated from these devices and tested. These PPD based devices had very similar properties to devices prepared with TPD and NPD. OLED devices were prepared by vapor deposition of a film of the hole transporter (TPD, NPD or PPD) onto an ITO coated glass substrate. A film of aluminumtris(8-hydroxyquinolate) was then evaporated onto the HTL film followed by a Mg-Ag cathode. Figure 2 shows current-voltage and current-light output curves of identical devices made with all three hole transporters. Reliability tests are being performed, but the elevated glass transition temperature is expected to increase the lifetimes of devices made with these materials relative to TPD or NPD.

Asymmetric molecules as hole transporters and crystallization inhibitors.

A general approach to making molecular materials which form stable glasses involves decreasing the degree of symmetry the molecule has. This lowering of symmetry makes it more difficult for the molecules to pack into a regular lattice and

** The T_g value for α -NPD has been checked in our lab, while the T_g for the β form has been pulled from the literature. We have recently prepared a sample of β -NPD to check the T_g . The asymmetric materials discussed below show very little difference in their thermal properties for the α and β isomers, so a big change in the NPD compounds seemed odd. The sample we have collected data on at this point needs to be purified further, but the preliminary T_g is actually much higher than α -NPD. We will include this data with the remaining thermal data for the compounds that still need to be purified in Tables 1 and 2.

slows or eliminates crystallization. A related approach is to add low levels of dopants (*i.e.* different molecular species) to retard crystallization of the molecular solid. This can be seen in a number of different studies of materials for OLEDs. We found in the initial studies of CBP (Figure 1) that we could grow glassy thin films that had very promising properties as a hole transporter in Alq based devices. When we scaled up the synthesis of CBP and purified it the material was found to crystallize immediately on deposition. We could not make the glassy form of the material at all. The reason for this is that the initial experiments were carried out with CBP which had a 2-5% carbazole impurity in it. This impurity prevented crystallization. We have now designed and synthesized molecules that will utilize asymmetry to form stable glasses and we hope to use these materials as tailored dopants to hinder crystallization in other molecular materials. Many of the materials studied here were prepared specifically for doping into CBP. In particular they are constructed with a carbazole group at one end and a different amine at the other. The idea was that the carbazole end would interact strongly with CBP, while there will be less interaction with the other amine group, leading to a hindrance to crystallization.

The amine compounds prepared thus far are shown in Tables 1 and 2. Table 1 has materials built around a single phenylene core (*i.e.* amine- C_6H_4 -amine), while those in Table 2 are built around a 4,4' biphenylene core (*i.e.* amine- C_6H_4 - C_6H_4 -amine). The thermal properties for these materials are listed with them in the tables. The compounds have a range of T_g values from 50 to 125°C. Some of these materials have high T_g values (*e.g.* compounds **XI** and **XII**), and are excellent candidates as HTL materials by themselves. The thermal behavior for these asymmetric materials are all very similar, as illustrated in Figure 3 for compound **XII**. On the first heating cycle only a melting transition is observed at 291°C. The sample is then cooled to room temperature and heated again. On the second heating cycle a T_g is observed at 125°C followed by a crystallization transition at 180°C and a melt transition at same temperature as before. If the sample is heated through the T_g, but not the recrystallization the cycle can be repeated several times. If however the sample is heated through the recrystallization and cooled, a T_g is not observed on subsequent reheating. The explanation for this behavior is that the sample is in a crystalline form on removing it from the sublimation tube. This is not a surprise since the rate of cooling in the sublimation is very slow. On heating the sample through the melt and then cooling rapidly to room temperature a glass is formed. If this glass is heated through the crystallization transition the sample converts from a glass to a crystal. If the sample is not heated through the recrystallization transition the sample remains a glass. Similar behavior is observed for all of the asymmetric materials

(with transitions at different temperatures of course). We are scaling up the synthesis of compounds **XI** and **XII** to make OLED with each of these materials as the HTL.

In order to examine how these asymmetric materials will perform as crystallization inhibitors we examined a range of different compositions of an asymmetric HTL and CBP. In these experiments the asymmetric HTL and CBP are mixed and ground together with a mortar and pestle to form a relatively homogeneous sample. When this mixture is heated in the differential scanning calorimeter (DSC) we observe two melt transitions, one for the asymmetric material and one for CBP. Figure 4 shows DSC scans for a mixture of compound **I** and CBP (10% compound **I** by weight). The sample in the DSC pan at this point is a solution of compound **I** in CBP. The sample is cooled from the melt and on reheating we see a Tg of 107°C and a recrystallization transition at 145°C. A melt is then observed at 285°C. The thermal behavior for compounds **I**- **XII** all give the same thermal behavior, with the same Tg and recrystallization temperatures as observed for mixtures shown in figure 4. We have also examined mixtures with different ratios of the asymmetric HTL to CBP. We see the same thermal behavior for these mixtures as we saw for the 10% mixture, *i.e.* a Tg of 110-115°C and recrystallization and melt transitions. We plan to make OLEDs from one of these mixtures by two different methods. In one case we will vapor deposit the materials simultaneously from two sources, in the other case we will prepare a mixture which sublimes as a stable ratio.

Table 1:


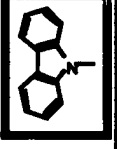
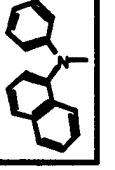
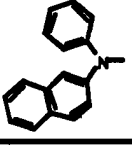
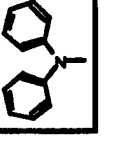
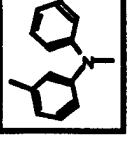
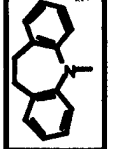
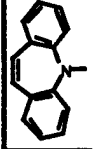
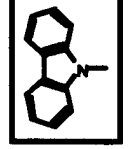
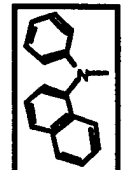
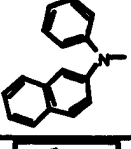
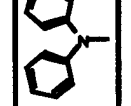
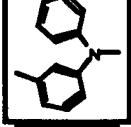
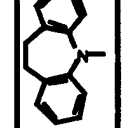
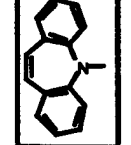
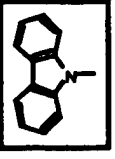
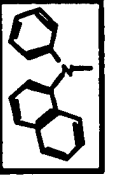
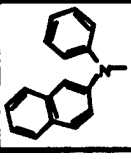
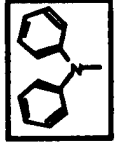
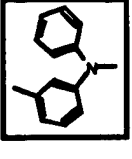
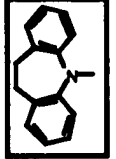
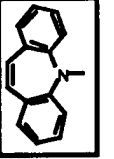
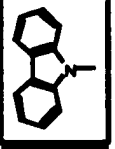
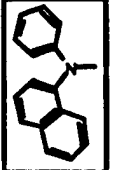
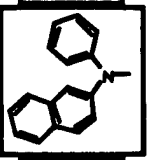
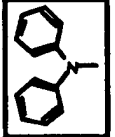
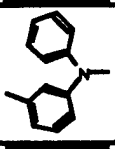
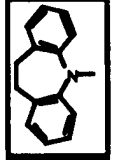
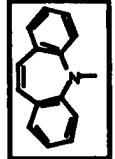
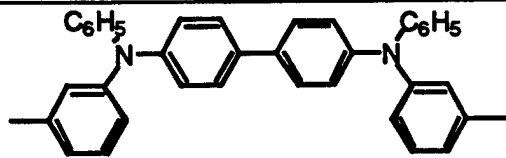
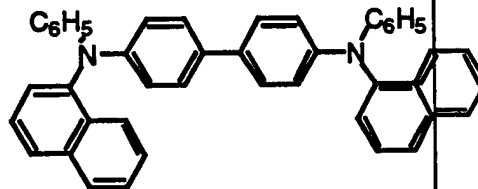
							
	Mp = 310 Tg = NA	Mp = 215° Tg = 88° I	Mp = Tg = 83° II	Mp = Tg = 61° III	Mp = Tg = 54° IV	Mp = 233° Tg = 91° V	Mp = 25° Tg = 10° VI
		Mp = 185° Tg = 70°	prepared, needs purification	prepared, needs purification	prepared, needs purification	prepared, needs purification	sublime no DSC yet
				prepared, needs purification			
						prepared, needs purification	prepared needs purification
							
							prepared needs purification
							

Table 2:

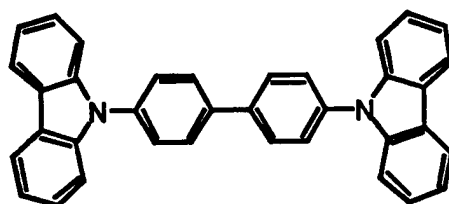
							
	Mp = 290° Tg = NA	Mp = Tg = 109° VII	Mp = Tg = 107° VIII	Mp = Tg = 91° IX	Mp = Tg = X	Mp = 273° Tg = 117° XI	Mp = 291 Tg = 125° XII
		Mp = 265° Tg = 100°	prepared, needs purification	sublimed no DSC yet	prepared, needs purification	prepared, needs purification	prepared, needs purification
				prepared, needs purification	prepared, needs purification	prepared, needs purification	prepared, needs purification
					prepared, needs purification	prepared, needs purification	prepared, needs purification
					Mp = 175° Tg = 60°	prepared, needs purification	
						prepared, needs purification	prepared, needs purification
							



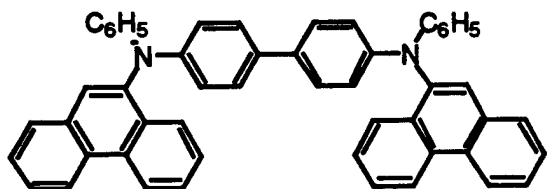
TPD - well known



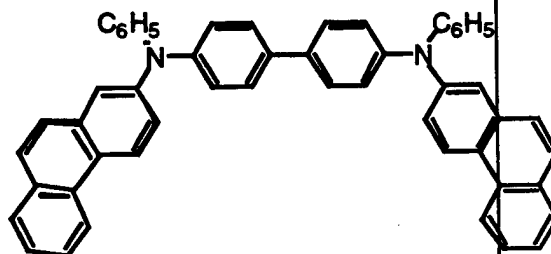
NPD - Kodak/Sato



CBP - ours



PPD - ours



Kodak cpd.

Figure 1: These are the symmetric compounds referred to above. We have indicated those compounds that are uniquely ours and those that have been described by other people.

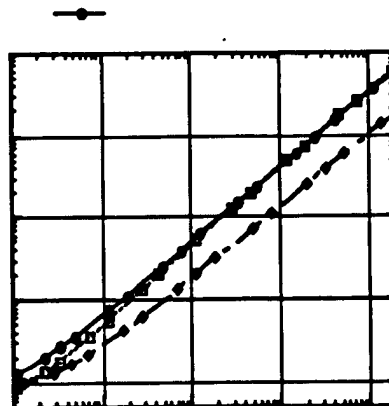
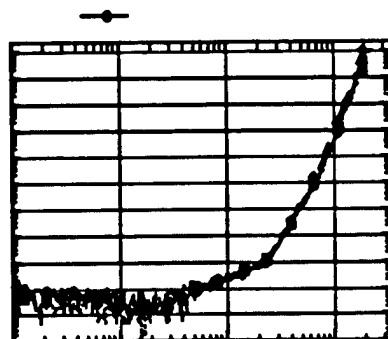
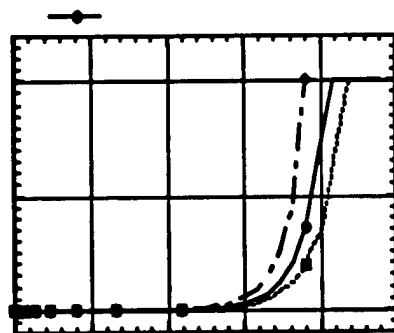


Figure 2: TPD, NPD and PPD OLED data.

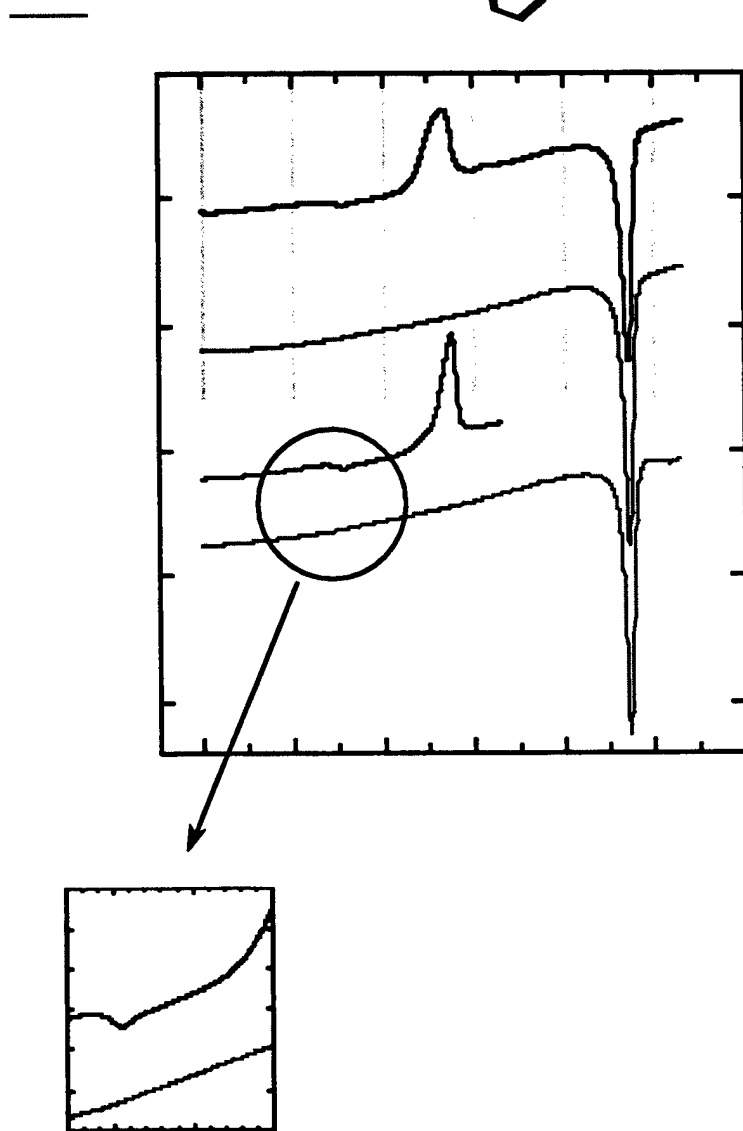
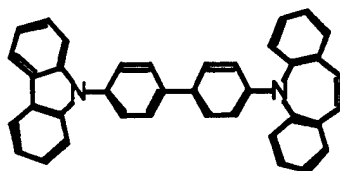


Figure 3: First DSC scan of compound **XII**, shows melt at 290°C. Second DSC scan of compound **XII**, show a Tg of 125°C, after which there is a crystallization at approximately 175°C. The scan was stopped at 230°C, before the melt at 290°C. Third DSC scan shows only the melt of the crystalline form at 290°C. Fourth DSC scan again shows the Tg at 125°C, along with the crystallization and melt as before. Since scan #4 went completely through the melt, the cooled compound was once able to form into the glassy state.

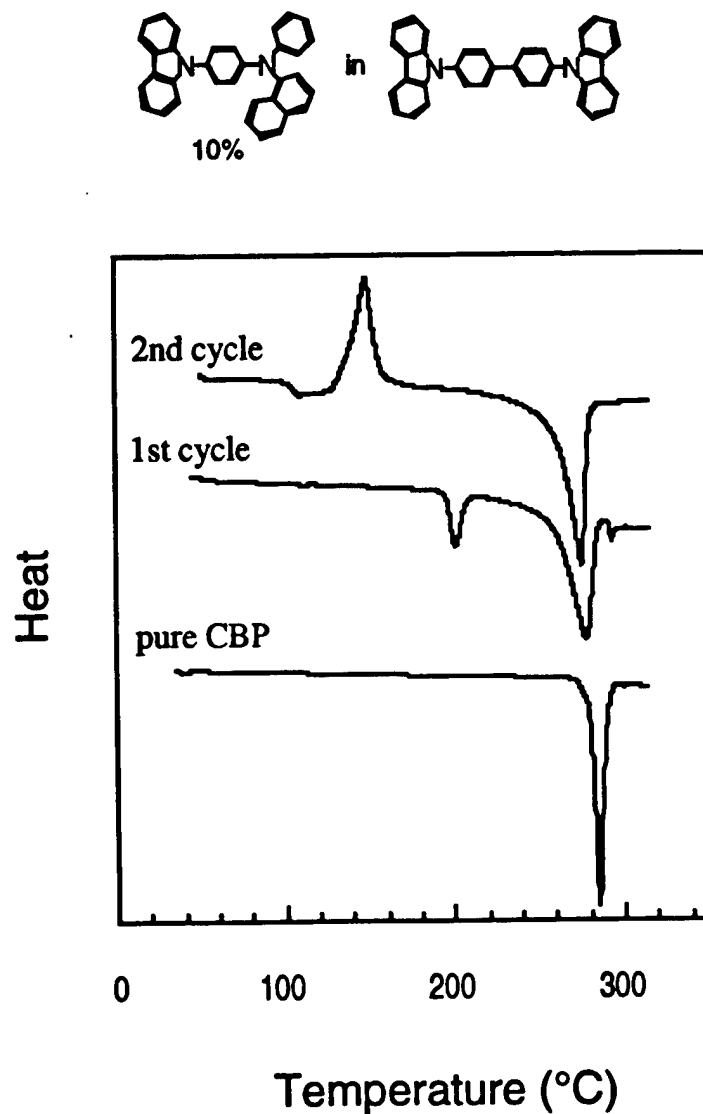


Figure 4: First DSC scan of a mixture of CBP and 10 % compound I. Lower melt transition is due to compound I, while the second transition is due to CBP. Second DSC scan of the same mixture gives a glass transition at 107°C, after which there is a crystallization at approximately 145°C, along with a melt of CBP at 280°C. Note that the asymmetric compound I, stays a glass and does not crystallize as shown from the absence of the melt corresponding to it.

TPP doped OLEDs

This is already covered in the two color OLED section of this report, but is discussed in more detail here.

Electroluminescence from a fluorescent dye doped into Alq₃ involves a critical energy transfer from an excited Alq₃ molecule to the dye dopant molecule. The most efficient way to affect this energy transfer is a Förster energy transfer process.^{1,2} Förster energy transfer involves a dipole-dipole coupling of the transition dipole moments for excited Alq₃ and the dye in its ground state. As Alq₃ relaxes its energy is transferred directly to the dye molecule, Figure 2(a). For this discussion we will refer to the excited molecule as the donor (of energy) and the dye as the acceptor (of energy). The advantage of this sort of energy transfer process is that the dipole-dipole interaction can be quite strong over large distances, allowing efficient energy transfer over distances of 30 Å or more. In order to assess the efficiency of such a process it would be useful to be able to evaluate the rate of energy transfer relative to radiative relaxation of the donor (Alq₃ exciton). A high rate of energy transfer relative to radiative relaxation will lead to emission exclusively from the dye dopant. An analytical expression for the rate of Förster transfer has been derived, but is difficult to apply to randomly doped systems such as those used in OLEDs. The problem arises from the fact that the dipole-dipole interaction and thus the energy transfer will have a strong distance dependence. The broad distribution of distances in the randomly doped sample would lead to a broad distribution of rates. A more common approach to evaluating Förster energy transfer is to calculate the Förster radius, R_0 , given in Equation 1(a). The Förster radius is defined as the distance between the donor and acceptor at which the probability of intermolecular energy transfer equals that of relaxation of the donor by fluorescence or other means. A large Förster radius is indicative of a very efficient energy transfer process, which will compete with fluorescence very effectively at distances shorter than R_0 . A short Förster

¹ A. Gilbert and J. Baggott, *Essentials of Molecular Photochemistry*, Blackwell Scientific Publications, Oxford, 1st edn., 1991, p.173.

² J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, a division of John Wiley and Sons Ltd, London, 1970, p. 569.

radius is indicative of a very inefficient process that requires very short donor-acceptor distances to be effective. In Equation 1 κ^2 is an orientation factor, which has a value of $2/3$ for random donor-acceptor orientations as found in doped OLEDs, n is the refractive index of the medium, N_A is Avagadro's number. $F_M(\tilde{\nu})$ is the fluorescence spectrum of the donor, defined as in Equation 1(b), where Φ_{PL} is the fluorescence quantum yield and $\epsilon_Q(\tilde{\nu})$ is the molar decadic extinction coefficient spectrum of the acceptor, and $\tilde{\nu}$ is the energy in wavenumbers.

Figure 2: (a) Schematic representation of Förster energy transfer. (b) overlap integral from Equation 1 shown as the shaded region of the curves.

Equation 1

$$R_0^6 = \frac{0.5291\kappa^2}{n^4 N_A} \int_0^\infty F_M(\tilde{\nu}) \epsilon_Q(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4}$$

(a)

$$\Phi_{PL} = \int_0^\infty F_M(\tilde{\nu}) d\tilde{\nu}$$

(b)

The absorption spectrum of TPP and EL spectrum of Alq₃ show a high degree of overlap of the two spectra. The Förster radius for energy transfer from excited Alq to TPP is 33 Å (n of Alq₃ = 1.7 • (TPP) = $2.26 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at 516 nm). This is a relatively large radius for energy transfer in this doped material. At a doping level of 0.3% there is 34 Å between TPP molecules on average, thus the maximum distance an Alq₃ exciton can be from a TPP molecule is roughly 17 Å, which is well below the Förster energy transfer radius. A high degree of energy transfer is expected even at low doping levels, as observed in TPP doped OLEDs.

Novel host materials for blue OLEDs

We have investigated a new host material for doped organic LEDs. $X_2\text{Al}(2\text{-}o\text{-phenoxy-pyridine})$ complexes, where the X ligands could be a number of different alkoxides, give narrow blue fluorescence. Devices prepared with this material give very weak blue electroluminescence, with very poor I-V characteristics. [diphenyl-bispyrazolylborate]₃Al (DPBA) is a colorless material which emits weakly in the blue to purple part of the spectrum. LEDs fabricated with this material as the hole transporting

medium (*i.e.* ITO/DPBA/Alq/Mg•Ag) are very inefficient. If DPBA is used as an electron transporter with a TPD hole conductor (*i.e.* ITO/TPD/DPBA/Mg•Ag) electroluminescence is not observed. Very efficient blue electroluminescence is observed, however, when a device is prepared with a TPD hole transporter and an electron transporting emissive layer prepared with a mixture of X₂Al(2-*o*-phenoxy-pyridine) and DPBA (*i.e.* ITO/TPD/emitter/Mg•Ag). This doped OLED gave good blue emission. We have looked at a range of different mixtures with different ratios of DPBA to dopant. Unfortunately, the DPBA host proved to be unreliable. Sublimation of this material led to decomposition and nonuniform deposition. We are currently examining the doping of the phenoxy-pyridine dopant into other hosts for blue EL.

Doped aluminum quinoxaline complexes

We have focused on trying to develop improved host materials for red OLEDs. The devices we have focused on involve devices made with fluorescent dyes doped into electron transporting materials, such as Alq₃. In addition to giving good control over the color of the emitted light, emission from dopants in OLEDs can lead to a significant narrowing of emission. An example of this is the doping of tetraphenylporphine (TPP) into Alq. The emission from Alq is centered at 510 nm and is 100 nm wide at half-height. The TPP doped device gives saturated red emission ($\lambda_{\text{max}} = 650 \text{ nm}$) with a width of 40 nm. The narrowing of the spectrum comes from the fact that the dyes are isolated and do not form aggregate or excimeric states. The EL spectra are very similar to those observed in dilute solution.

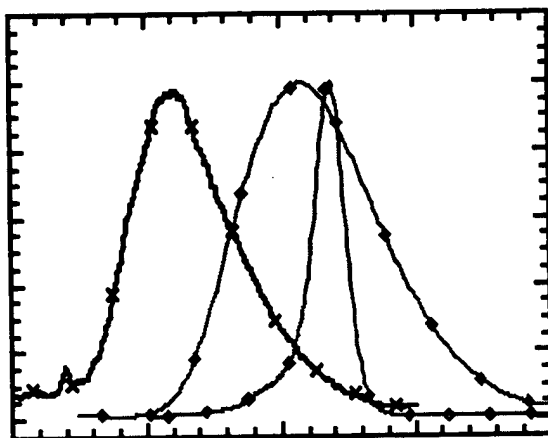
In many cases a change of host material is required to match the host with the dye dopant. For example we found that when an squarilium dye, which gives narrow red luminescence, is doped into Alq, the device emits predominantly from the Alq (see figure 1). The problem in this combination is that the energy match of Alq and the dye is very poor, leading to very inefficient exciton transfer from the Alq host to the dye. We have found that if we match the host and dopant energies well, efficient energy transfer to the squarilium dopant can be observed. This is shown for a significantly red shifted analog of Alq, aluminumtris(8-hydroxy-quinoxaline), Alx, in figure 1.

We have prepared, purified and begun our detailed studies of Alx (figure 2) as a host for predominantly red organic light emitting diodes. The Alx is used as a doped host material and electron transporter. Emission in a device of this type comes from the dye dopant and leads to more efficient electroluminescence as described by our group and others.

Alx gives orange photoluminescence with a PL maximum at 580 nm, which is significantly red shifted relative to aluminumtris(8-hydroxy-quinoline), Alq (PL max at 515 nm). This red shift is important for achieving a high level of energy transfer from the host material to a red fluorescent dye dopant. The IV data shown in Figure 3 are noisy at low current (due to instrumental problems and not OLED related problems), but show the expected shape in their $\log(I)$ - $\log(V)$ plots (device is ITO/TPD/Alx/Mg-Ag). The close similarity of the I-V characteristics for doped and undoped devices show the dye dopant is not perturbing the electrical properties of the device as expected for a dopant in low concentration. The EL spectrum from a device prepared with Alx is shown in figure 4. The device emits orange light, with a line width comparable to that of Alq. In order to shift the emission from this device to the red we have examined the doping of a novel fluorescent dye into this material. We have investigated indigo and an inner salt (figure 2) as dopants for Alx. To the best of our knowledge this is the first time these fluorescent dyes have been used in an OLED and the first time Alx has been used as a host. The EL spectrum of this doped device is shown in figures 1 and 4 and shows the predominantly red emission achievable with this dopant. If this dopant is used with Alq relatively little red light is emitted and EL emission is dominated by Alq at all doping levels. The energy match between Alx and the dye is very good and leads to efficient energy transfer. In Alq the energy match is poor and gives nearly all of the emission from the Alq. We have also prepared and are examining the Zn and Mg derivatives of 8-hydroxyquinoxoline. They give PL spectra identical to that observed for Alx. We are currently purifying these materials and will examine them in OLEDs in the near future.

In addition we have recently prepared the Ga analog of Alx. Its emission spectrum is shown in figure 5. This compound give a significant red shift relative to Alx. We are currently scaling up the synthesis to make enough material to examine this Ga complex in OLEDs.

—x—



—x—

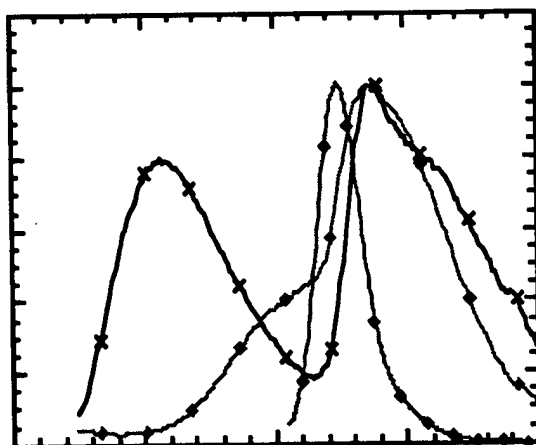
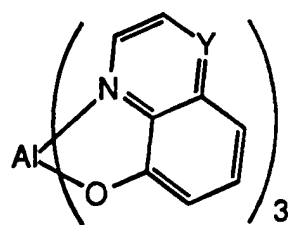
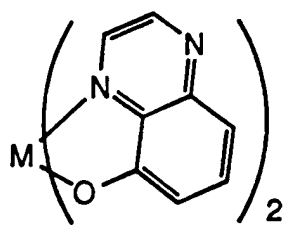


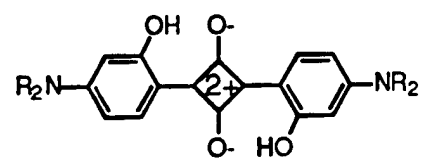
Figure 6: emission from doped Alq and Alx devices.



Alx: R = N
Alq: R = CH



M = Zn, Mg



inner salt - dopant

Figure 7: Alx, Alq, red dopant and zinc and Mg complexes.

IV characteristics of doped and undoped Alx OLEDs

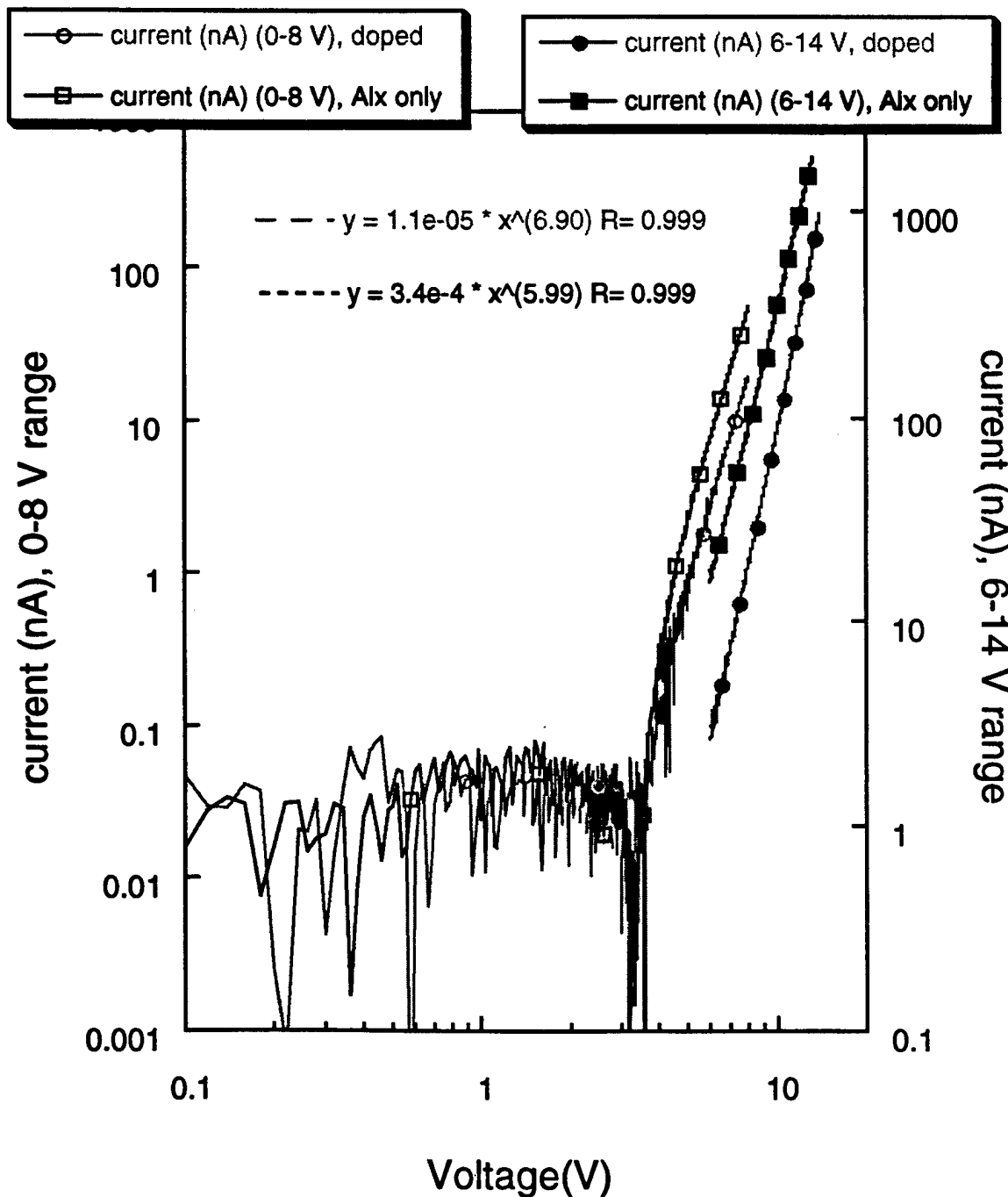


Figure 8: IV plots for Alx and doped Alx devices.

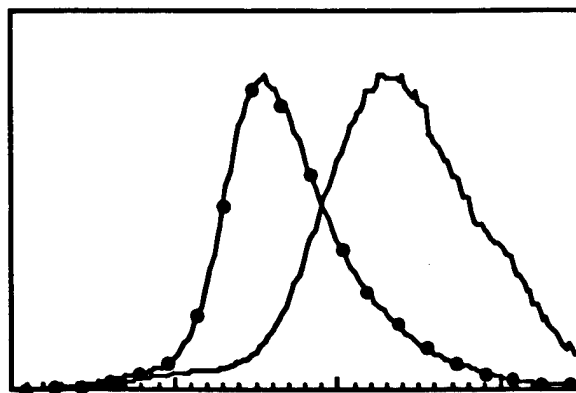
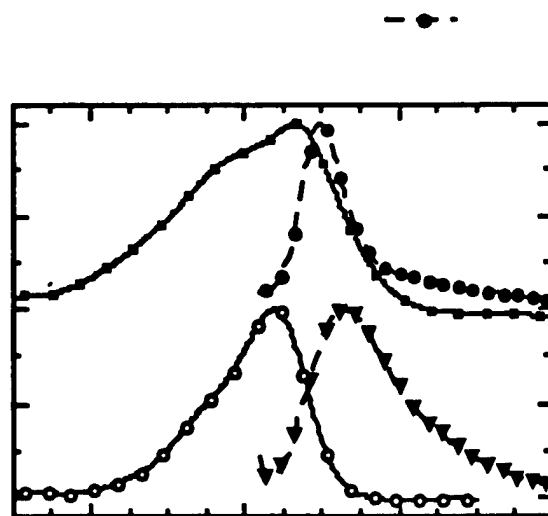


Figure 9: EL spectra of Al_x and doped Al_x OLEDs.

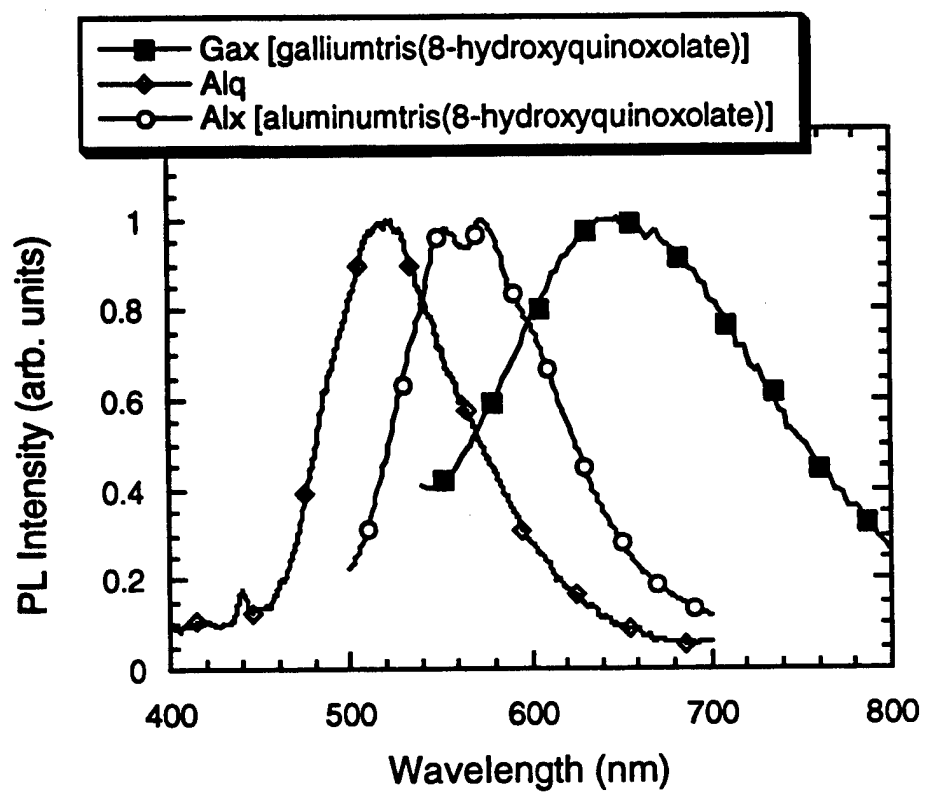


Figure 10: Photoluminescence spectra of Alq, Alx and Gax

Section 4:

Final Technical Report

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Executive Summary

Organic Light Emitting Devices (OLEDs) are the key components in the development of a new class of flat panel display technology. In contrast to III-V semiconductor-based emissive devices, OLEDs have the following advantageous properties;

- Inexpensive to manufacture due to the simplicity of the deposition process using abundant and standard chemicals
- High resolution because of the unique single RGB pixel
- Fully compatible with silicon electronics
- Capable of being conformal to surfaces due to their ability to deposit on top of flexible and transparent substrates

The team at the Hughes Research Laboratories, Inc (HRL) has worked very closely with the team at Princeton and USC to carry out the objectives of the program. Specifically, HRL has

- successfully transferred the technology of fabricating OLEDs from Princeton University
- demonstrated the world's first alphabetic logos and 8 by 12 array
- carried out accelerated lifetime studies of packaged OLEDs, up to 1000 hrs of operation
- developed an understanding of the fundamental limitation to brightness
- worked with Delco Electronics on detailed commercial reliability test requirements and benchmarks

Key technical issues that are open for investigation, and were not part of this program

- Structural stability of the OLEDs as function of temperature
- Practical limits of input drive current to maintain a degree of brightness
- Detailed understanding of the chemical physics of contacts
- Packaging mechanics for long lifetimes (>10,000 hrs)

Hughes Research Labs, Inc. (HRL), in its participation in this program, has successfully transferred the technology of fabricating organic light-emitting devices (OLEDs) from Princeton University to HRL. In addition, we have made numerous improvements to the OLED and demonstrated several novel displays. These displays include alphabetic logos and multiple-pixel arrays with emission from one face or from both faces (semi-transparent devices). Highlights of these accomplishments are described in the following paragraphs.

Our goals have been to 1) evaluate discrete devices fabricated by Princeton University, 2) transfer the OLED fabrication technology from Princeton to HRL, and 3) improve the OLEDs for greater reliability and efficiency. We have achieved all of these goals. In addition, we have also exceeded the final goal of the program by demonstrating a 2-dimensional 8 x 12 array of OLED pixels. We have performed this work at an accelerated pace in order to capture marketing opportunities and to ensure the continued leadership position of our team in the rapidly advancing area of OLED technologies.

(A) Technology Transfer from and to Princeton University, and Demonstration of the World's First Transparent Alphabetical Display

Several samples of discrete OLEDs fabricated at Princeton were evaluated at HRL. As a result of these evaluations, we have focused our efforts on making several specific improvements to the OLEDs. First, we have developed a more manufacturable approach to the fabrication of devices. In order to make the devices easier to test, we established a fixed, basic design for the size of test samples and for the contact-electrode patterns on those samples. This has permitted us to use machined fixtures and interchangeable masks in the device fabrication as well as simple contact pins and clamps in the test setups and demonstration units. The OLED samples are 0.75" x 0.75" in size and can have a light-emitting area as large as 0.4" x 0.4". These samples have been designed to be compatible with the evaluation setups at Delco Electronics.

Fabrication of the OLEDs includes processing steps done at HRL as well as at Princeton. The basic OLED that we make contains layers of ITO (the anode); an insulator (for some designs); organic materials - the hole-transporting layer (HTL), electroluminescent layer (EL) and electron-transporting layer (ETL); MgAg (the cathode) and a covering conductor (either Ag or ITO). The ITO and insulator layers are processed at HRL. The organic materials, cathode and covering conductor are deposited at Princeton. After these layers are deposited, a glass cover piece is placed over the sample and sealed along its perimeter by an adhesive, to enclose the reactive OLED materials.

As a second area of focus, we have investigated several different sealants in an attempt to improve the shelf life and operating lifetime of OLEDs. We identified 4 different materials, all are low-outgassing epoxies and vacuum sealants, and compared them with the sealant used by Princeton. Two of the sealants - epoxies from TraCon and EpoTek - demonstrated operation lifetimes that are at least as good as the results obtained with the Princeton sealant, another EpoTek epoxy. However, examination of samples sealed with those 3 sealants show dark spots that have developed after 6 months of storage. We investigated two other sealants - another TraCon epoxy and a vacuum seal compound.

We have made numerous trips to Princeton for the device processing and fabrication efforts. Over 130 samples have been fabricated. As a result of this extensive effort, we have identified various improvements to the OLED structure and fabrication process. Improvements we made have been focused toward reducing the series resistance, reducing the operating voltage, reducing the likelihood of short or open circuits, and increasing the integrity of contact pads. We reduce the series resistance by increasing the thickness of the Ag covering conductor from 50 nm to 150-200 nm. This additional covering also improves the long-term integrity of the MgAg contact by protecting it from corrosion. To improve the contact pads, we deposit a metal such as Ag or Au over the anode contact pad areas so that the electrical connection need not be made to the ITO. Such pads are amenable to wire bonding and are resistant to scratching. We reduce the operating voltage by controlling carefully the Mg to Ag ratio of the cathode and by ensuring that the deposition is done in a high vacuum. We also limit the exposure

of the ITO anode surface to high temperatures, reactive gases and chemical etchants. We reduce the likelihood of electrical shorts and opens by adjusting the layer thicknesses and patterning methods.

These design and process improvements have also increased our yield of good devices. We consistently fabricate devices that have an operating voltage of 6-8 volts, comparable to the best results reported for OLEDs whose organic layers consist of TPD and Alq. Lower voltage operation can be achieved by using other materials for the organic layers. We have applied our process and design improvements in the fabrication of several types of OLED samples. One sample type, used for comparing process and design modifications and for lifetime tests, contains 4 separate OLEDs that are separately addressed. A maximum of 4 samples can be processed in a single fabrication run. This has permitted us to make side-by-side evaluations of processing parameters and test conditions.

A second type of sample contains alphabetic displays of Hughes and Delco logos, as shown in Figure 1. We have found these samples of great use in marketing the OLEDs. We have demonstrated "standard" displays, for which the light is emitted through the glass substrate. We have also demonstrated semi-transparent displays, for which the light is also emitted through the cathode contact. As an example of the effectiveness of our collaboration with Princeton, HRL successfully demonstrated a first-ever transparent logo display shortly after Princeton demonstrated the first transparent OLEDs. We then suggested process improvements which aided Princeton to demonstrate first-ever transparent 11-segment alphanumeric displays.

(B) Demonstration of 8 by 12 Pixel Displays

One goal of this 2.5-year program is the development of an 8x8 pixel display by the Princeton/Hughes/USC team. We demonstrated single-color (green) 8x12 pixel displays as shown in Figure 2. In contrast to the row-and-column addressed displays reported recently by Pioneer, these displays have separate connections for each pixel. Since each illuminated element of the display has power applied continuously rather than being scanned, the instantaneous drive power to each pixel can be much lower. Furthermore, our design can be extended simply to versions that contain integrated driving and switching electronics. The displays we demonstrated have 400x400 micron pixels that have a spacing of 500 microns. Both displays with "standard" OLEDs and transparent OLEDs have been demonstrated. By applying the process and design improvements described above, we have achieved displays with operating voltages below 10 V, operating currents of 10-20 μ A, and series resistances of approximately 100 Ω .

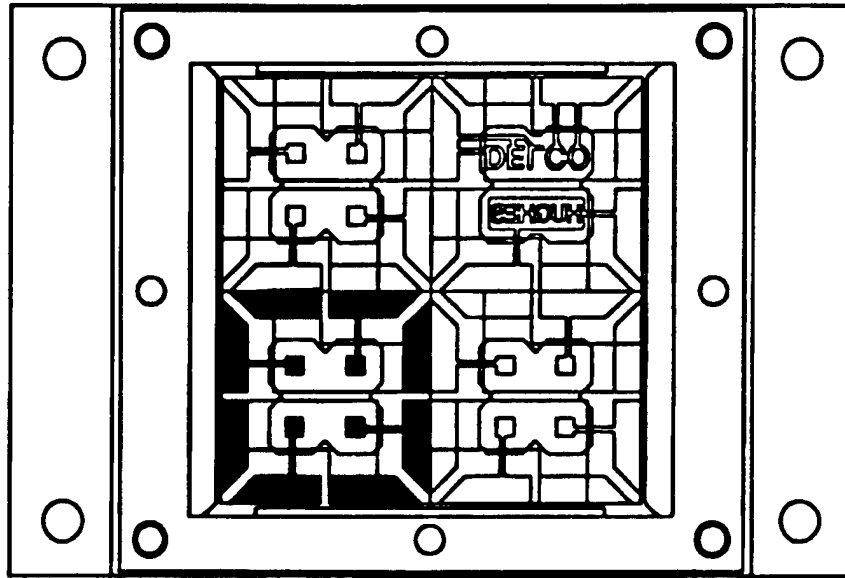


Figure 1. Machined fixture holding 3 OLED test cells plus a alphabetic logo display.

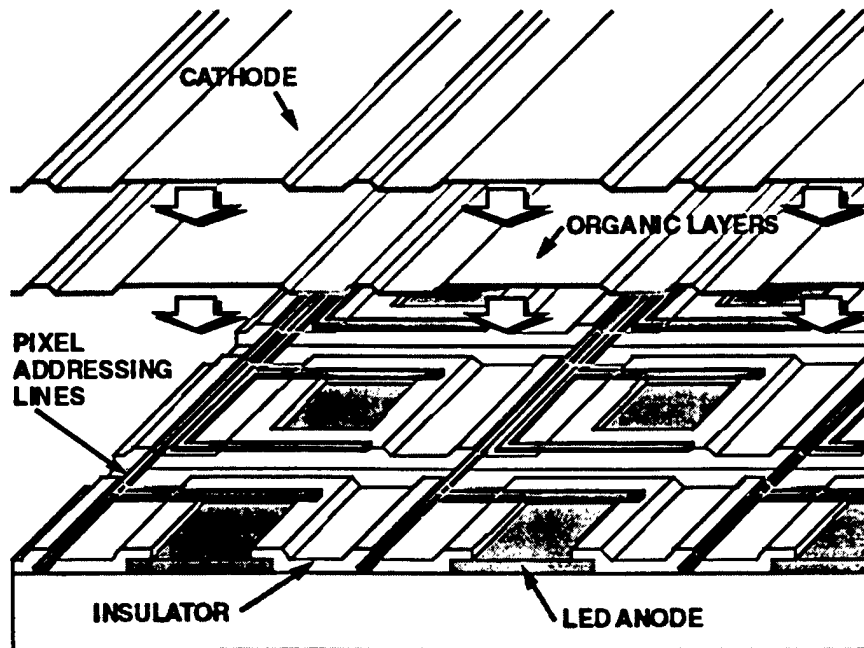


Figure 2. Illustration of individually addressed, multiple pixel array demonstrated this year.

(C) OLED Lifetime Study

During the course of this program, we set up an OLED lifetime characterization laboratory. This laboratory was dedicated to testing OLED operating lifetime, power efficiency and optical spectral response. The equipment included an optical integrating sphere, a computer, a humidity chamber, and a test stage for the operating lifetime stress

tests. Also, in parallel to setting up the lab, we developed a software program for the operation of the OLED lifetime tests.

To test the validity of the lifetime measurement set up, we have performed a number of preliminary accelerated lifetime stress experiments by applying a constant current, 400 mA/cm^2 on OLEDs that were fabricated at Princeton. This current level is more than an order of magnitude higher than the normal operation of OLEDs: using it to stress the device, we think we can better our understanding of the OLED degradation mechanisms. So far, our early lifetime stress data explains that the current conduction through the organic emitting layer is very much influenced by the storage of the trapped electrons. It also suggests that the charge storage is definitely one of the degradation mechanisms in OLED.

We applied the theory of charge injection into insulators, and found that a hopping charge transport mechanism explains the I-V characteristics during current injection. In addition, we also found that as traps get permanently filled, the carrier transport process can be described in terms of space-charge- limited conduction. Eventually, this process leads to the quenching of the optical emission due to either filled traps and/or degradation processes along the metal-organic interface.

Princeton was supplied with substrates deposited with ITO and a mask set specifically designed to produce devices compatible with our testing facility. The details concerning the fabrication of the devices was reported in our March 11, 1997 Quarterly Report. I-V curves, brightness (cd/m^2), efficiency (lumen/driving electrical wattage), and spectral emission were measured for each device. Lifetime tests were then made on the devices by driving the OLED at a constant current of 0.38 ma (15 ma/cm^2). The bias voltage and optical output were then recorded as a function of time. The results of these measurements were reported in our March 11, 1997 Quarterly Report. In addition, they were also reported at the April 29, 1997 meeting held at Princeton and the viewgraphs that were presented there are included along with this report.

It is speculated that the poor device performance (reduced lifetimes; maximum found with devices tested at HRL was $\sim 700 \text{ hr}$) recorded in our devices may be associated with the degradation that was visually observed at the organic-ITO interface. It appears that the thin-film organic layer separated from the substrate following device operation for approximately 200 hr. This may be a consequence of inadequate substrate preparation prior to organic thin-film deposition and/or the failure to properly hermetically seal the device following fabrication from the ambient.

Benchmark against other display technologies

	Emission Wavelength [nm]	FWHM [nm]	External Quant Eff.	Power Eff.
InGaN Blue LED Nichia [1]	450	20	8.7%	8%
InGaN Green LED Nichia [2]	525	45	2.1%	1.7%
Green OLED Kodak [3]	550	118	1%	0.5%
Green OLED Sanyo [4]	580	75	4.5%	1.7%

Remarks:

- [1] S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, Appl. Phys. Lett., **67** (1995) 1867.
- [2] S. Nakamura, M. Senoh, N. Iwasa, and S. Nagahama, Jpn. J. Appl. Phys. **34** (1995) L824-L826.
- [3] C. Wang and S.A VanSlyke, Appl. Phys. Lett. **51** (1987) 913.
- [4] Y. Hamada, T. Sano, K. Shibata and K. Kuroki, Jpn. J. Appl. Phys. **34** (1995) L824-L826.

Section 5.

Refereed Publications Partially Supported by DARPA

- [1] "Reliability and Degradation of Organic Light Emitting Devices." P.E. Burrows, V. Bulovic, S.R. Forrest, L.S. Sapochak, D.M. McCarty and M.E. Thompson, *Appl. Phys. Lett.* **65**, 2922 (1994).
- [2] "Poly(P-Phenylene Vinylene)/Tris (8-Hydroxy)Quinoline Aluminum Heterostructure Light Emitting Diode." C.C. Wu, J.K.M. Chun, P.E. Burrows, J.C. Sturm, M.E. Thompson, S.R. Forrest and R.A. Register, *Appl. Phys. Lett.* **66**, 653 (1995).
- [3] "Photoluminescence Efficiency and Absorption of Aluminum-Tris-Quinolate (Alq3) Thin Films." D.Z. Garbuzov, V. Bulovic, P.E. Burrows and S.R. Forrest, *Chem. Phys. Lett.* **249**, 433 (1996).
- [4] "Temperature Dependence of Current Transport and Electroluminescence in Vacuum Deposited Organic Light Emitting Devices." Z. Shen, P.E. Burrows, V. Bulovic, D.M. McCarty, M.E. Thompson and S.R. Forrest, *Jpn. J. Appl. Phys.* **35**, L401 (1996).
- [5] "Relationship Between Electroluminescence and Current Transport in Organic Heterojunction Light Emitting Devices." P.E. Burrows, Z. Shen, V. Bulovic, D.M. McCarty, S.R. Forrest, J.A. Cronin and M.E. Thompson, *J. Appl. Phys.* **79**, 7991 (1996).
- [6] "Transparent Organic Light Emitting Devices." V. Bulovic, G. Gu, P.E. Burrows, M.E. Thompson and S.R. Forrest, *Nature* **380**, 29 (1996).
- [7] "Transparent Organic Light Emitting Devices." G. Gu, V. Bulovic, P.E. Burrows, S.R. Forrest and M.E. Thompson, *Appl. Phys. Lett.* **68**, 2606 (1996).
- [8] "Systematic Study of the Photoluminescent and Electroluminescent Properties of Pentacoordinate Carboxylate and Chloro Bis(8-Hydroxyquinoline) Complexes of Gallium (III) L.S. Sapochak, P.E. Burrows, D. Garbuzov, D.M. Ho, S.R. Forrest, M.E. Thompson, *J. Phys. Chem.* **100**, 17766-17771 (1996).
- [9] "Vacuum-Deposited, Non-Polymeric Flexible Organic Light Emitting Devices." G. Gu, P.E. Burrows, S. Venkatesh and S.R. Forrest, *Optics Letters*, **22**, 172 (1997).
- [10] "Color-Tunable Light Emitting Devices." P.E. Burrows, S.R. Forrest, S.P. Sibley and M.E. Thompson, *Appl. Phys. Lett.* **69**, 2959 (1996).
- [11] "Organic Films Deposited on Si p-n junctions: Accurate measurements of fluorescence internal efficiency, and Application to Luminescent Antireflection Coatings." D.Z. Garbuzov,

S.R. Forrest, A.G. Tsekoun, P.E. Burrows, V. Bulovic and M.E. Thompson, J. Appl. Phys. **80**, 4644 (1996).

[12] "High External Quantum Efficiency Organic Light Emitting Devices." G. Gu, D.Z. Garbuzov, P.E. Burrows, S. Venkatesh and S.R. Forrest, Opt. Lett. **22**, 396 (1997).

[13] "A Surface-Emitting, Vacuum-deposited Organic Light Emitting Device." V. Bulovic, P. Tian, P.E. Burrows, M.R. Gokhale, S.R. Forrest and M.E. Thompson, Appl. Phys. Lett. **70**, 2954 (1997).

[14] "Transparent Flexible Organic Light Emitting Devices." G. Gu, Z. Shen, P.E. Burrows and S.R. Forrest, Adv. Mat. **9**, 725 (1997).

[15] "Achieving Full Color Organic Light Emitting Devices for Lightweight, Flat Panel Displays." P.E. Burrows, G. Gu, V. Bulovic, S.R. Forrest and M.E. Thompson, IEEE Trans. Elec. Dev. **44**, 1188 (1997).

[16] "Three-color Organic Light Emitting Devices." Z. Shen, P.E. Burrows, V. Bulovic, S.R. Forrest and M.E. Thompson, M. E. Science **276**, 2009 (1997).

[17] "Saturated Three Color Organic Light Emitting Devices." P. E. Burrows, Z. Shen and S. R. Forrest, 1997 Int. Display Research Conf., Toronto, 1997; p 318.

[18] "Low Pressure Organic Vapor Phase Deposition of Small Molecular Weight Organic Light Emitting Device Structures." M.A. Baldo, V.G. Kozlov, P.E. Burrows, S.R. Forrest, V.S. Ban, B. Koene and M.E. Thompson, Appl. Phys Lett. **71**, 3033 (1997).

[19] "Photolithographic Patterning of Vacuum-Deposited Organic Light Emitting Devices." P.F. Tian, P.E. Burrows and S.R. Forrest, Appl. Phys. Lett., **71**, 3197 (1997).

[20] "A Metal-free Cathode for Organic Semi-conductor Devices." G. Parthasarathy, P.E. Burrows, V. Khalfin, V.G. Kozlov, and S.R. Forrest, App. Phys. Lett., **72**, 2138 (1998).

Invited Book Chapters and Reviews

[21] "Organic Emitters Make Possible New Generation of Displays." S.R. Forrest, P.E. Burrows and M.E. Thompson, Laser Focus World, (*February* 1995).

[22] "Prospects and Applications for Organic Light Emitting Devices." P.E. Burrows, S.R. Forrest and M.E. Thompson, Curr. Opin. Solid State Mat. Sci. **2**, 236 (1997).

[23] "Growth and Characterization of Electroluminescent Display Devices Using Vacuum-Deposited Organic Materials." in "*Organic Electroluminescent Materials and Devices*", ed. S. Miyata and H.S. Nalwa. (1996).

Section 6

U.S. Patents Pending and Issued

- [1] "Mixed Vapor Deposited Films For Electroluminescent Devices," S. Forrest, M. Thompson, P. Burrows, D. McCarty.
- [2] "Transparent Contacts for Organic Devices," S. Forrest, P. Burrows, V. Bulovic, G. Gu. (Issued: 12/30/97).
- [3] "Displays Having Mesa Pixel Configuration," S. Forrest, P. Burrows, D. Garbuzov.
- [4] "Light Emitting Device with Stack of OLEDs and Phosphor Down Converter," S. Forrest, P. Burrows, D. Garbuzov. (Issued: 2/24/98).
- [5] "Multicolor Display Devices," S. Forrest, M. Thompson.
- [6] "Bright Red Organic LED," S. Forrest, P. Burrows, M. Thompson.
- [7] "Red-Emitting Organic Devices (OLEDs)," S. Forrest, P. Burrows, M. Thompson.
- [8] "Driving Circuit for Stacked Organic Light Emitting Devices," S. Forrest, P. Burrows. (Issued: 5/26/98).
- [9] "Vacuum Deposited, Non-Polymeric Organic LEDs," S. Forrest, P. Burrows, G. Gu.
- [10] "Stacked Organic Light Emitting Devices," S. Forrest, P. Burrows.
- [11] "An Improved Method for Depositing Indium Tin Oxide Layers in organic Light Emitting Devices," S. Forrest, P. Burrows, Z. Shen.
- [12] "OLEDs Containing Thermally Stable Asymmetric Charge Carrier Materials," M. Thompson, B. Koene, D. Loy.
- [13] "Method of fabricating and Patterning OLEDs," S. Forrest, P. Burrows, P. Tian.
- [14] "High Efficiency Coumarin-Doped OLEDs," S. Forrest, P. Burrows, M. Thompson.
- [15] "An Organic Light Emitting Device Containing a Hole Injection Enhancement Layer," S. Forrest, M. Thompson, P. Burrows, V. Bulovic.
- [16] "Organic Light Emitting Devices Containing a Metal Complex of 5-Hydroxy-Quinoxaline as a Host Material," P. Burrows, S. Forrest, M. Thompson, A. Shoustikov, Y. You.
- [17] "High Contrast Transparent OLED Display," S. Forrest, P. Burrows, M. Thompson.

- [18] "Saturated Full Color Stacked Organic Light Emitting Devices," S. Forrest, P. Burrows, Z. Shen.
- [19] "Organic Semi-Conductor Laser," V. Kozlov, P. Burrows, S. Forrest.
- [20] "Double Heterostructure Infrared and Vertical Cavity Surface Emitting Lasers," V. Kozlov, P. Burrows, S. Forrest.
- [21] "Stacked OLEDs for High Brightness Light Source," P. Burrows, S. Forrest.
- [22] "Fluorescent Dye Dopants Based on Jelly Fish Chromophore," M. Thompson, Y. You, N. Petasis.
- [23] "Saturated, Efficient Red Organic Light Emitting Devices," S. Forrest, V. Bulovic, V. Kozlov.
- [24] "Method for Deposition and Patterning of Organic Thin Films," V. Bulovic, P. Burrows, S. Forrest.
- [25] "Improved Electrodes for Organic Light Emitting Devices," S. Forrest, P. Burrows, M. Shtein (San Jose).
- [26] "Highly Transparent Electroluminescent Organic Light Emitting Device," S. Forrest, P. Burrows, G. Parthasarathy.